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(54) Title: SPHERICAL MICROPARTICLES COMPRISING A NUCLEATION PROMOTER AND BIOLOGICALLY ACTIVE COMPOUNDS

(57) Abstract

The present invention relates to spherical microparticles comprising biologically active compounds and a nucleation promoter within the microparticles. The invention also relates to a process for their preparation, to the use thereof for the preparation of a composition for controlling plant pests, weeds or animals parasites, and to aqueous spray mixtures containing the novel microparticles.

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Spherical microparticles comprising a nucleation promoter and biologically active compounds

The present invention relates to spherical microparticles comprising biologically active compounds and a nucleation promoter within the microparticles. The invention also relates to a process for their preparation, to the use thereof for the preparation of a composition for controlling plant pests, weeds or animal parasites, and to aqueous spray mixtures containing the novel microparticles.

The microencapsulation of active ingredients in polymeric materials with different polymers is known and can be carried out by various methods, as described for example in Encyclopedia of Polymer Science, John Wiley Sons, 1968, Vol. 8, pp. 719-736.

Some typical microencapsulation methods are: coacervation, interfacial polymerisation at liquid-liquid surfaces or interfacial polycondensation, for example at a solid phase boundary. In addition to these chemical methods, other suitable methods are physical methods such as the microencapsulation of aerosols. Amino resins are often used as polymeric encapsulating materials for microparticles that contain agrochemical compounds. An overview of the broad field of use of these resins for microencapsulation is given, inter alia, in Acta Polymerica 40, (1989) No. 4, pp. 243-251.

Particular demands are made of the release properties of biologically active agrochemicals. On the one hand, the applied microparticles must be comparably active in field application to e.g. emulsifiable concentrates. In addition, they shall release the active ingredient uniformly over an extended period of time. On the other hand, virtually no active ingredient shall be released on skin contact, so that a high degree of handling safety is ensured.

The preparation and properties of microparticles prepared with self-crosslinking amino resins are described in Acta Polymerica 40, (1989) No. 5, pp. 325-331. In the processes referred to therein, the starting materials are solid compounds which are e.g. additionally ground to give a fine dispersion in the aqueous polymer solution and are then encapsulated. The drawback of this process is that the solid materials have to be ground to an average particle size of c. 10-30 µm. In addition, usually large amounts of fine dust that have to be reagglomerated are formed. The addition of active ingredients in the liquid, dissolved or melt state is therefore usually of interest.

One problem that arises in the preparation of microcapsules from the melt or in solution is the recrystallisation of the active ingredients in the microcapsule. The active ingredient is first frozen in its liquid state, resulting in an amorphous core having different physical properties than in the crystalline state. During recrystallisation, long crystal needles or large irregularly shaped crystals may form. Some of these crystals pierce the capsule wall and thereby nullify the advantages of the microencapsulation, at least partially. This recrystallisation may also not occur until during storage.

This recrystallisation can have such a pronounced effect on the stability to hydrolysis, on the dispersing properties during the preparation of spray mixtures, on the flow properties of the microcapsules and on the release properties of the active ingredient that the microcapsules are unfit for use.

It has now been found that these drawbacks can be eliminated if the microcapsules comprise, in addition to the active ingredient, a nucleation promoter that effects a rapid recrystallisation of the fused active ingredient in the microcapsule and ensures that only small microcrystallites form that remain almost wholly encapsulated by the capsule wall. Premature release of the active ingredient is thereby prevented, the handling safety is ensured, and the release properties remain effective enough to achieve sufficiently good activity. Long-term stability is good, as the recystallisation no longer occurs during storage.

The active ingredient is released approximately uniformly over an extended period of time from the microparticles, so that a good activity is achieved.

In one of its aspects therefore the invention relates to essentially spherical microparticles comprising a biologically active compound which is solid and crystalline at room temperatue as core substance and a polymeric capsule material, which microparticles additionally comprise a nucleation accelerator.

Suitable nucleation promoters are mainly linear polymers. Regardless of the active ingredient, the nucleation promoter may suitably be a polyester, a polyacrylate, a polyamide, a polyolefin, a polyvinyl alcohol, a polyvinyl pyrrolidone or a polyether. Those skilled in the art will easily find suitable combinations by simple experimentation by mixing and fusing the components as well as subsequent determination of the crystal

size, conveniently by microscopy.

A preferred nucleation promoter is a polyethylene glycol or a polyethylene glycol which is etherified with C_1-C_8alkyl radicals at the OH end groups, a polyvinyl pyrrolidone or a polyvinyl alcohol.

The average molecular weight of the polyethylene glycols is preferably 10 000 to 40 000, most preferably 20 000 to 35 000.

If a polyvinyl alcohol is used, the degree of hydrolysis is preferably greater than 75 %, most preferably 95 to 100 %.

The average molecular weight of the polyvinyl alcohol is preferably 120 000 to 200 000.

If a polyvinyl pyrrolidone is used, the average molecular weight is preferably higher than 10 000.

The polymeric nucleation promoters can be used in an amount of 0.5 to 30 % by weight, preferably of 1 to 5 % by weight, based on the weight of the active ingredient.

The spherical microparticles preferably have an average diameter of!0.5 to 500 µm. More preferably the microparticles have an average diameter of 0.5 to 100 µm and, most preferably, of 0.5 to 20 µm.

The polymeric wall material is preferably 5 to 40 % by weight of the total weight of the microparticles.

The polymeric wall material may consist of a polyacrylate, a polyurea, a polyurethane, a polyester or an amino resin.

The polymeric wall material is preferably an amino condensation resin, most preferably a polycondensate of melamine and formaldehyde, a wholly or partially etherified melamine-formaldehyde condensate, a urea-formaldehyde condensate, a urea-glutaraldehyde condensate or a benzoguanamine-formaldehyde condensate.

The molar ratios of urea to formaldehyde are 1:2.5 to 1:3.5, preferably 1:2.7 to 1: 3.2.

If glutaraldehyde is used instead of formaldehyde, the molar ratios may be 1:1.5 to 1:2.5, preferably 1:1.8 to 1: 2.2.

The molar ratios of melamine to formaldehyde can be 1:3.5 to 1:8, preferably 1:4 to 1:6. The degree of etherification of these resins can be adjusted by the molar ratio of melamine to methanol and is typically c. 1:10 to 1:20, preferably c. 1:15 to 1:18.

Suitable amino resins for forming microparticles will be found, inter alia, in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, Vol. 2, pp. 440-469.

The polycondensate is most preferably a melamine-formaldehyde condensate, a wholly or partially etherified melamine-formaldehyde condensate, or a urea-formaldehyde condensate.

The biologically active compound is preferably a pesticide or a mixture of pesticides, and is most preferably a herbicide, an insecticide, an acaricide, a nematicide, an ectoparasiticide, a fungicide or a mixture thereof.

Typical examples of pesticides are: urea derivatives, triazines, triazoles, carbamates, phosphoric acid esters, dinitroanilines, morpholines, acylalanines, pyrethroids, benzilic acid esters and polycyclic halogenated hydrocarbons.

Specific examples of pesticides suitable for use in the practice of this invention are listed hereinbelow (common names as given in The Pesticide Manual, 9th Edition, British Crop Protection Council):

<u>Urea derivatives</u>
Chlorbromuron, chloroxuron, chlorotoluron, fluometuron, thiazafluron and triasulfuron.

<u>Halogenated acetanilides</u>
Dimethachlor, alachlor, propachlor.

<u>s-Triazines</u>
Atrazine, propazine, terbuthylazine, ametryn, aziprotryne, cyromazine.

Triazole derivatives
Etaconazole, 1-[2-(2,4-dichlorophenyl)-pent-1-yl]-1H-1,2,4-triazole, triadimefon, difenoconazole.

Carbamates
Dioxacarb, aldicarb, benomyl.

Phosphoric acid esters
Methidathion, anilofos, azinphos methyl, fenamiphos, azamethiphos.

Dinitroanilines
Benfluralin, pendimethalin, butralin, fluchloralin.

Acylalanines
Metalaxyl, fluralaxyl, benzoylprop ethyl, flamprop methyl.

Pyrethroids
Cypermethrin, resmethrin, tetramethrin.

Benzilic acid esters
Bromopropylates, chlorobenzilates, chloropropylates.

Miscellaneous
Bromoxynil, ioxynil, oxadiazon, dicofol, fenoxycarb.

Preferred pesticides are S-2,3-dihydro-5-methoxy-2-oxo-1,3,4 thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate (= methidathion), 2-phenylamino-4-methyl-6-cyclopropylpyrimidine and 3-(3-chloro-p-tolyl)-1,1-dimethylurea = chlorotoluron.

The microparticles may additionally contain a hydrophobic wax. The hydrophobic wax may be a natural wax, a modified natural wax, or a semi-synthetic or fully synthetic wax.

The addition of wax, which is fused together with the active ingredient to form a melt which is added to the aqueous solution, has for its object to form a wax film that surrounds the active ingredient on the inner microcapsule wall. Penetration of water into the capsule core is thereby hindered, while the release properties remain effective enough to achieve

sufficiently good activity.

The wax is preferably a vegetable wax, an animal wax, a montan wax, a paraffin wax, a polyolefin wax or an amide wax. Most preferably the hydrophobic wax is a macrocrystalline paraffin wax, a microcrystalline paraffin wax or a polyethylene wax.

The wax preferably has a melting point of 30 to 80°C.

In a preferred embodiment of the invention, the wax is used in an amount of 1 to 20 % by weight, most preferably of 5 to 15 % by weight, based on the biologically active compound or mixture thereof in the microcapsules.

In another of its aspects, the invention relates to a process for encapsulating biologically active compounds in the form of essentially spherical microcapsules, comprising the steps of
a) preparing an aqueous solution of surfactants, catalysts and monomers, prepolymers or polymers which are suitable for forming a capsule wall,
b) forming an emulsion or dispersion of the substantially water-insoluble biologically active compound or mixture thereof in the solution a) by adding said biologically active compound or mixture thereof under high shear force, and
c) forming a solid capsule wall around the biologically active compound or mixture thereof,
which process comprises blending the biologically active compound or mixture thereof with a nucleation promoter before forming the emulsion or dispersion b), fusing the blend and adding the melt so obained to the solution a).

A preferred embodiment of the process comprises fusing the the biologically active compound or mixture thereof and the nucleation promoter together and adding the co-melt to tie reaction solution a) at a temperature which is higher than that of said reaction solution a).

Another preferred embodiment of the process comprises dissolving the nucleation promoter in a solvent, adding the solid active ingredient and cautiously evaporating the solvent, with stirring, to give an active ingredient powder which is coated with the nucleation promoter and which can likewise be fused and added direct to the reaction solution.

If a wax is used in addition to the nucleation promoter, then the active ingredient, the nucleation promoter and the wax are preferably blended, the blend is fused, and the melt so obtained is added to the reaction mixture a).

The aqueous solution may contain, in addition to the monomers, prepolymers or polymers that form the capsule wall, one or more than one water-soluble monomer, oligomer or polymer as emulsifier or dispersant. Suitable emulsifiers or dispersants are anionic, cationic or nonionic substances. The surfactants customarily used in formulation technology are described, inter alia, in the following publications:

"Mc Cutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, NJ, USA, 1988",

H. Stache, "Tensid-Taschenbuch" (Handbook ofSurfactants), 2nd edition, C. Hanser Verlag Munich, Vienna 1981,

M. and J. Ash. "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-1981.

The surfactants are polyethylene glycols, polyethylene glycol monoalkyl ethers, polyethylene glycol-polypropylene glycol copolymers, polyvinyl pyrrolidones and acrylic acid-acrylamide copolymers.

The polymers used as surfactants usually have a lower molecular weight than that of the polymers used as nucleation promoters. This applies in particular to the polyethylene glycols and polyethylene glycol ethers.

Methods of producing high shear forces are known per se. It is preferred to use a high-speed impeller or a rotary homogeniser.

In another of its aspects, the invention relates to a process for controlling plant pests, weeds or animal parasites, which comprises suspending the novel microparticles in a biologically active concentration in water and applying the suspension so obtained to the pests or to the locus thereof.

In yet another of its aspects, the invention relates to the use of the novel microparticles for the preparation of a composition for controlling plant pests, weeds or animal parasites, and to water-dilutable powders, water-dispersible granules or aqueous spray mixtures containing said microparticles.

The invention is illustrated by the following Examples.

Examples for the preparation of the precondensates.

Example A1: Preparation of a modified melamine-formaldehyde precondensate
With stirring, 28 g of melamine (0.22 mol) are added to 124 ml of a 30 % aqueous solution of formaldehyde. The reaction mixture is adjusted with 1 N aqueous NaOH to pH 9 and heated to 94°C, whereupon the melamine dissolves while reacting with the aldehyde. The reaction mixture is then cooled to 62°C and, after addition of 120 ml of methanol (3.75 mol) and 7 ml of a 15 % aqueous solution of hydrochloric acid, the reaction is carried out at 62°C for 30 minutes. Then 2.8 g of triethanolamine are added and the azeotropic mixture of methanol-water is distilled from the reaction mixture. After adjustment to a solids content of c. 40 to 60 % by weight, 6 g of urea are added to the solution, which is then cooled to room temperature.

Example for the preparation of the microparticles.

Example B1: 60 ml of water and 3 g of the precondensate prepared according to Example A1 as well as 0.15 g of polyethylene glycol (molecular weight 300) are charged to a reactor with temperature control. The reaction mixture is heated to 60°C and acidified with 2.1 ml of 2N aqueous citric acid. Then 12.6 g of methidathion and 0.945 g (7.5 %, based on the active ingredient) of polyethylene glycol (mol wt 20 000) are fused together, homogenised and heated to 60°C. The melt is added rapidly to the reaction mixture, with stirring (Ultraturrax, 12 000 rpm), and stirred for 10 minutes at this speed. Stirring is afterwards continued with a paddle agitator at 500 rpm for 120 minutes at 60°C. The mixture is then cooled to give a suspension of fine particles having average diameters of 1 to 10 µm. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder.
Thermoanalytical measurements show that the active ingredient is mainly present in microcrystalline form in the capsule core.

Example B2: The procedure of Example B1 is repeated, but using 0.252 g of polyethylene glycol (mol wt 20 000), corresponding to 2 %, based on the active ingedient. The mixture is cooled to give a suspension of finely particulate spherical particles having a diameter of 1 to 10 µm. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder.
Thermoanalytical measurements show that the active ingredient is mainly present in microcrystalline form in the capsule core.

Example B3: The procedure of Example B1 is repeated, but using 0.63 g of polyethylene glycol (mol wt >30 000, degree of hydrolysis 95 %), corresponding to 5 %, based on the active ingedient. The mixture is cooled to give a suspension of finely particulate spherical particles having a diameter of 1 to 10 µm. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder.
Thermoanalytical measurements show that the active ingredient is mainly present in microcrystalline form in the capsule core.

Example B4: The procedure of Example B1 is repeated, but using 0.63 g of polyethylene glycol (mol wt >10 000), corresponding to 5 %, based on the active ingedient. The mixture is cooled to give a suspension of finely particulate spherical particles having a diameter of 1 to 10 µm. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder.
Thermoanalytical measurements show that the active ingredient is mainly present in microcrystalline form in the capsule core.

Example B5: The procedure of Example B1 is repeated, but using in addition to 0.252 g of polyethylene glycol (mol wt 20 000), corresponding to 2 %, based on the active ingedient, 1.26 g of paraffin wax having a melting point of >40°C. The mixture is cooled to give a suspension of finely particulate spherical particles having a diameter of 1 to 10 µm. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder.
Thermoanalytical measurements show that the active ingredient is mainly present in microcrystalline form in the capsule core.

What is claimed is:

1. Spherical microparticles comprising a biologically active compound which is solid and crystalline at room temperatue as core substance and a polymeric capsule material, wherein the microparticles additionally comprise a nucleation accelerator.

2. Spherical microparticles according to claim 1, wherein mainly a linear polymer is used as biologically active compound.

3. Spherical microparticles according to claim 1, wherein the nucleation promoter is a polyester, a polyacrylate, a polyamide, a polyolefin, a polyvinyl alcohol, a polyvinyl pyrrolidone or a polyether.

4. Spherical microparticles according to claim 1, wherein the nucleation promoter is a polyethylene glycol or a polyethylene glycol which is etherified with C_1-C_8alkyl radicals at the OH end groups, a polyvinyl pyrrolidone or a polyvinyl alcohol.

5. Spherical microparticles according to claim 4, wherein the average molecular weight of the polyethylene glycol is 10 000 to 40 000.

6. Spherical microparticles according to claim 4, wherein the average molecular weight of the polyethylene glycol is 20 000 to 35 000.

7. Spherical microparticles according to claim 4, wherein the average molecular weight of the polyvinyl alcohol is 120 000 to 200 000.

8. Spherical microparticles according to claim 4, wherein the average molecular weight of the polyvinyl pyrrolidone is higher than 10 000.

9. Spherical microparticles according to claim 1, wherein the polymeric nucleation promoter is used in an amount of 0.5 to 30 % by weight, based on the weight of the active ingredient.

10. Spherical microparticles according to claim 1, wherein the polymeric nucleation promoter is used in an amount of 1 to 5 % by weight, based on the weight of the active

ingredient.

11. Spherical microparticles according to claim 1, which have an average diameter of 0.5 to 500 µm.

12. Spherical microparticles according to claim 1, which have an average diameter of 0.5 to 100 µm.

13. Spherical microparticles according to claim 1, which have an average diameter of 0.5 to 20 µm.

14. Spherical microparticles according to claim 1, wherein the polymeric wall material is 5 to 40 % of the total weight of the microparticles.

15. Spherical microparticles according to claim 1, wherein the polymeric wall material is a polyacrylate, a polyurea, a polyurethane, a polyester or an amino resin.

16. Spherical microparticles according to claim 1, wherein the polymeric wall material is an amino condensation resin.

17. Spherical microparticles according to claim 15, wherein the polycondensate is a melamine-formaldehyde condensate, a wholly or partially etherified melamine-formaldehyde condensate, a urea-formaldehyde condensate, a urea-glutaraldehyde condensate, a benzoguanamine-formaldehyde condensate, or a urea-glyoxal condensate.

18. Spherical microparticles according to claim 16, wherein the polycondensate is a melamine-formaldehyde condensate, a wholly or partially etherified melamine-formaldehyde condensate or a urea-formaldehyde condensate.

19. Spherical microparticles according to claim 1, wherein the biologically active compound is a pesticide or a mixture of pesticides.

20. Spherical microparticles according to claim 19, wherein the biologically active compound is a herbicide, an insecticide, an acaricide, a nematicide, an ectoparasiticide, a fungicide or a mixture thereof.

21. Spherical microparticles according to claim 20, wherein the biologically active compound is selected from S-2,3-dihydro-5-methoxy-2-oxo-1,3,4 thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate (= methidathion), 2-phenylamino-4-methyl-6-cyclopropylpyrimidine and 3-(3-chloro-p-tolyl)-1,1-dimethylurea (=chlortoluron).

22. Spherical microparticles according to claim 1, which additionally comprise a natural wax, a modified natural wax, a partially synthetic or a fully synthetic wax.

23. Spherical microparticles according to claim 22, wherein the wax is a vegetable wax, an animal wax, a montan wax, a paraffin wax, a polyolefin wax or an amide wax.

24. Spherical microparticles according to claim 22, wherein the wax is a macrocrystalline paraffin wax, a microcrystalline paraffin wax or a polyethylene wax.

25. Spherical microparticles according to claim 22, wherein the wax has a melting point in the range from 30 to 80°C.

26. Spherical microparticles according to claim 22, wherein the wax is present in the capsule in an amount of 1 to 20 % by weight, based on the biologically active compound or mixture thereof.

27. Spherical microparticles according to claim 22, wherein the wax is present in the capsule in an amount of 5 to 15 % by weight, based on the biologically active compound or mixture thereof.

28. A process for encapsulating a biologically active compound in the form of essentially spherical microcapsules, comprising the steps of
a) preparing an aqueous solution of surfactants, catalysts and monomers, prepolymers or polymers which are suitable for forming a capsule wall,
b) forming an emulsion or dispersion of the substantially water-insoluble biologically active compound or mixture thereof in the solution a) by adding said biologically active compound or mixture thereof under high shear force, and
c) forming a solid capsule wall around the biologically active compound or mixture thereof,
which process comprises blending the biologically active compound or mixture thereof

with a nucleation promoter before forming the emulsion or dispersion b), fusing the blend, and adding the melt so obained to the solution a).

29. A process according to claim 28, which comprises fusing the biologically active compound or mixture thereof and the nucleation promoter together and adding the co-melt blend to the reaction solution a) at a temperature which is higher than that of said reaction solution a).

30. A process according to claim 28, which comprises blending the active ingredient, the nucleation promoter and the wax, fusing the blend, and adding the melt so obtained to the reaction mixture a).

31. A method of controlling plant pests, weeds or animal parasites, which comprises suspending microparticles as claimed in claim 1 in a biologically active concentration in water and applying the suspension so obtained to the pests or to the locus thereof.

32. The use of microparticles as claimed in claim 1 for the preparation of a composition for controlling plant pests, weeds or animal parasites.

33. A water-dilutable powder, a water-dispersible granular formulation or an aqueous spray mixture containing microparticles as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

Internat[illegible]al Application No
PCT/EP 95/02726

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N25/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 380 325 (GRIFFIN CORP) 1 August 1990 see page 7, column 19-39 see claims ---	1-4
A	FR,A,2 332 053 (BAYER AG) 17 June 1977 see page 2, line 2-11 see page 3, line 12-33 see page 4, line 36 - page 5, line 4 see page 11, line 26-34 --- -/--	1,28,29, 31-33

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
16 November 1995	24. 11. 95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Dalkafouki, A

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 95/02726

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8908 Derwent Publications Ltd., London, GB; Class A97, AN 89-059198 & JP,A,01 013 002 (SUMITOMO CHEM IND KK) , 17 January 1989 see abstract -----	1,21

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